A computational study of 13-atom Ne-Ar cluster heat capacities

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Abstract

Heat capacity curves as functions of temperature were calculated using Monte Carlo methods for the series of $Ne_{13-n}Ar_n$ clusters ($0 \leq n \leq 13$). The clusters were modeled classically using pairwise additive Lennard-Jones potentials. The J-walking (or jump-walking) method was used to overcome systematic errors due to quasiergodicity. Substantial discrepancies between the J-walking results and those obtained using standard Metropolis methods were found. Results obtained using the atom-exchange method, another Monte Carlo variant for multi-component systems, also did not compare well with the J-walker results. Quench studies were done to investigate the clusters' potential energy surfaces. Only those Ne-Ar clusters consisting predominately of either one or the other component had lowest energy isomers having the icosahedral-like symmetry typical of homogeneous 13-atom rare gas clusters; non-icosahedral structures dominated the lowest-energy isomers for the other clusters. This resulted in heat capacity curves that were very much different than that of their homogeneous counterpart. Evidence for coexistence behavior different than that seen in homogenous clusters is also presented.

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I. INTRODUCTION

The investigations discussed in this report are the second part of a comprehensive study of 13-atom binary rare gas clusters; the first part examined the series of clusters $Ar_{13-n}Kr_n$ for $0 \leq n \leq 13$.[1] Thirteen-atom homogeneous[2-10] and heterogeneous[11-20] clusters have been the subject of many studies. The homogeneous rare gas clusters exhibit "magic number" effects[2,20-25] for many of their properties that are due in large part to their compact icosahedral ground state configuration. Because Ar and Kr have similar sizes (the Ar radius is about 11% smaller than the Kr radius), all the 13-atom Ar-Kr clusters also had icosahedral-like lowest-energy configurations that played dominant roles in their behavior. This size similarity resulted in two different categories of Ar-Kr isomers: topological isomers based on geometric structures that were similar to those of their homogeneous counterparts, and permutational isomers, which were based on the various rearrangements of the different component atoms within a topological form. Ne and Ar have quite different sizes (the Ne radius is about 19% smaller than the Ar radius). This results in many additional non-icosahedral isomers with energies similar to the icosahedral-like isomers, which dramatically alters the Ne-Ar cluster behavior compared to that of their Ar-Kr counterparts. The other major difference between Ne-Ar and Ar-Kr clusters is in their intermolecular potentials, where the Ne and Ar values are far more dissimilar compared to the Ar and Kr values ($\epsilon_{\text{Ne-Ne}}/\epsilon_{\text{Ar-Ar}} = 0.2982$, $\epsilon_{\text{Ar-Ar}}/\epsilon_{\text{Kr-Kr}} = 0.7280$).

Heat capacities have been useful for elucidating the nature of cluster solid-liquid "phase" transitions.[2,4-8,17,26-28] Heat capacity curves as functions of temperature for homogeneous 13-atom clusters are characterized by a very large peak in the solid-liquid transition region that is primarily a consequence of the large energy gap between the ground state icosahedral isomer and the higher energy non-icosahedral isomers.[2,4-8] Thirteen-atom Ar-Kr clusters have heat capacity curves that are mostly similar to the homogeneous cluster curve, but there are interesting differences arising from the effects of the permutational isomers, made manifest as an additional, very small, heat capacity peak occurring at very low temperatures.[1,17] This

feature, arising from the low-energy icosahedral-like permutational isomers, is reminiscent of order-disorder transitions known to occur in some bulk alloy materials.[17] For 13-atom Ne-Ar clusters, though, the large disparity in the Ne and Ar potential parameters results in qualitatively different heat capacity curves.

Cluster heat capacities are notoriously difficult to calculate accurately using simulation methods because of poor convergence due to the incomplete sampling of configuration space. This is especially so for heterogeneous clusters, where the inadequate mixing of the different component atoms can become problematic at lower temperatures, leading to large systematic errors. As with my previous Ar-Kr heat capacity studies, I used the J-walking (or jump-walking) method[6] to obtain the heat capacities to good accuracy. J-walking has been shown to greatly increase Monte Carlo convergence rates and overcome systematic errors due to incomplete sampling in several studies.[1,2,5,17,26−29] Despite the poor performance of the standard Metropolis method in calculating heat capacities, the results obtained from the method can still provide additional insights when compared with the J-walking results, and so I also calculated heat capacity curves for each Ne-Ar cluster using the standard Metropolis method, as well as with a modified version that augments binary cluster simulations by using atom-exchange methods to enhance the mixing of the components.[16]

I begin in Section II with a brief overview of the various computational methods I used. Section III first examines the structural properties of 13-atom Ne-Ar clusters, discusses the results obtained for their heat capacities and potential energies as functions of temperature, and then examines the results obtained from the quench studies. The results are also compared to their corresponding Ar-Kr results. Finally, in Section IV, I summarize my findings and discuss some of the insights provided by the Ne-Ar cluster results.

II. COMPUTATIONAL METHOD

The computational methods used in this work were mostly similar to the methods I used in my previous study of Ar-Kr clusters.[1] The following briefly summarizes the important

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points; the reader is referred to the previous work for a more detailed description.

Monte Carlo simulations were run for all clusters in the series $Ne_{13-n}Ar_n$ with $0 \leq n \leq 13$. The clusters were modeled by the usual pairwise additive Lennard-Jones potential. Table I lists the Lennard-Jones parameters.[30] The Ne-Ar interaction parameters were determined from the usual Lorentz-Berthelot mixing rules.[31] I have followed Lee, Barker and Abraham[32] and have confined the clusters by a perfectly reflecting constraining potential of radius R_c centered on the cluster's center of mass. To maintain a common set of boundary conditions throughout the survey, the constraining radius was identical for all the clusters studied, with $R_c = 3\sigma_{\text{Ar-Ar}}$. Analogous to the Ar-Kr study, the energies and heat capacities are expressed in reduced units in terms of the smaller atom interaction, with $V^* = V/\epsilon_{\text{Ne-Ne}}$ and $C_V^* = C_V/k_B$.

Standard Monte Carlo simulations of clusters based on the sampling algorithm proposed by Metropolis $et\ al.$[33] are known to suffer from systematic errors due to quasiergodicity,[34] the non-ergodic sampling that typically arises with configuration spaces that are comprised of several regions separated by large barriers. For certain temperature domains, this can lead to bottlenecks that effectively confine the sampling to only some of the regions, resulting in large errors.[31] J-walking addresses the problem of quasiergodicity by coupling the usual small-scale Metropolis moves to occasional large-scale jumps that move the random walker to the different regions of configuration space in a representative manner.[6] The large-scale jumps are governed by Boltzmann distributions generated at higher temperatures where the sampling is ergodic. As in my previous study of Ar-Kr clusters, the more common external file implementation of J-walking was used, with the J-walker distributions generated beforehand and stored in an external array for subsequent jump attempts.[35]

I also found it necessary to again run several shorter, independent J-walker trials, instead of the single longer run that is usually done for homogeneous clusters. The heat capacity results were very sensitive to small errors in the J-walker distributions, especially at the lower temperatures. These errors were a consequence of the large increase in the number of isomers arising from the extra permutational isomers in the binary cluster case, which

made obtaining representative samples that much more difficult. Therefore, I ran at least five separate J-walking trials, with each trial sampling from its own unique set of J-walker distributions, to ensure there were no significant systematic errors in the binary cluster heat capacity curves. For those clusters showing especially large deviations in their heat capacity curves at low temperatures, I ran ten trials to reduce the uncertainties in the peak locations and heights. The results for the separate trials were then combined and averaged, with the standard deviations taken as estimates of the uncertainty. As was done with the Ar-Kr calculations, the total walk length for each temperature was set at 10^6 passes of data accumulation. Fig. 1 shows the results for $Ne_{11}Ar_2$. As can be seen in the plot, the noise level in each curve is about the same magnitude as the differences between the curves over most of the temperature range, indicating that these walk lengths were sufficiently long for the desired level of accuracy. However, for the smaller heat capacity peak occurring at 0.4 K, the curves show a much greater variation, comparable to the peak height itself. The results for this cluster were the worst of the series, and while none of the other Ne-Ar clusters showed such large deviations, the deviations were mostly larger than those obtained for their Ar-Kr counterparts.

I again ran standard Metropolis simulations for each cluster. The Metropolis results provided a check of the J-walking results for those temperature regions where quasiergodicity was not a problem, and they provided additional insights into the underlying behavior for those regions where quasiergodicity was evident. Simulations for each temperature consisted of 10^5 warmup passes, followed by 10^7 passes with data accumulation. The temperature scans were started at the lowest temperature from the global minimum configuration, with the final configuration for each temperature then used as the initial configuration for the next temperature. The scans were continued well past the cluster melting region. Figure 1 also shows the Metropolis results for $Ne_{11}Ar_2$. As can be seen, substantial discrepancies due to quasiergodicity are evident in the low temperature region. The Metropolis curve was too low until about 6 K, after which it rose sharply to approach the J-walker curves. As a check, I repeated some of the points using walk lengths of 10^8 passes of data accumulation per point.

Even with these long walks, the Metropolis method was unable to give accurate results below 6 K, although the results for $T > 6$ K were in good agreement with the J-walker results (the results obtained for 10^7 passes remained slightly too low until about 9 K).

The inadequacy of the standard Metropolis algorithm for simulating heterogeneous clusters at very low temperatures has been noted previously. Tsai, Abraham, and Pound[16] developed a simple but effective strategy to help overcome these limitations by incorporating an atom exchange scheme in their Metropolis algorithm. The method enhances the mixing of clusters by occasionally attempting an exchange move where one of the atoms of one component is swapped with one of the atoms of another component. The atom-exchange method showed considerable improvement over the standard Metropolis method for Ar-Kr clusters in the very low temperature region. It was even able to partially reproduce the mixing-anomaly peaks that were completely absent in the Metropolis results, although the agreement with the J-walking results was only qualitative in these regions. I also ran atom-exchange simulations for all the Ne-Ar clusters. These were done in a manner similar to the standard Metropolis runs described previously, with an atom-exchange move between randomly selected Ne and Ar atoms attempted once after every pass of standard Metropolis moves. The results for $Ne_{11}Ar_2$ can also be seen in Fig. 1. In this case, the atom-exchange method did not provide any improvement over the standard Metropolis method.

At the lower temperatures associated with the cluster solid-liquid transition regions, the competition between the intermolecular forces and atomic sizes effects which isomeric structures play dominant roles in the cluster's behavior. Thus, information concerning the relative populations of the lower energy isomers encountered during a simulation at a given temperature can offer much insight into the nature of cluster dynamics.[36,37] The relative frequencies of occurrence for each isomer can be obtained from quench studies done during the simulation, where the assumption is that the distribution of minima found in the quenches indicates the likelihood of the system being associated with a particular isomer. That is, the quench distributions are a reflection of the relative phase volume of each catchment basin.[38] To obtain further insight into the role cluster structure plays, I also performed quench studies

on each of the clusters simulated. Steepest-descent quenches[36] were performed periodically on each cluster during one of its five J-walker trials to monitor the relative frequency of occurrence for the lower energy isomers as functions of temperature. For each temperature, quenches were undertaken every 1000 passes, providing 1000 quenched configurations for subsequent analysis. In each instance, quench trajectories were run until the relative energy difference converged to within 10^{-7}.

Having a complete listing of all the stable low-energy isomers for a given cluster would also be valuable. Although the local minima comprising a typical cluster potential hypersurface are far too numerous to be completely catalogued in any practical manner, a reasonably complete listing of the important lower energy isomers can be obtained easily from the J-walker distributions. Since the distributions generated at a given temperature contain representative samples of a cluster's configuration space, a crude, but nonetheless effective, way to identify cluster isomers is to simply quench a sufficient number of the configurations stored in the distributions, saving them in an external file indexed by their energy, and then removing the duplicate configurations. This was done for all the clusters examined in this study. Again, each configuration was quenched until the relative energy difference converged to within 10^{-7}; the final composite file of unique isomers was then further refined by running another set trajectories until the relative energy difference converged to within 10^{-12}. For 13-atom Ar-Kr clusters, the low energy isomers in the quenched distributions were dominated by icosahedral-like structures having the smaller Ar atom in the center. This was not the case for the Ne-Ar clusters, though. $Ne_{12}Ar$ and $Ne_{11}Ar_2$ both had Ne-core icosahedral-like structures as their lowest-energy isomers, but for most of the other clusters, almost all of the expected Ne-core icosahedral-like permutational isomers were absent from the quenched distributions. This implies that these isomers played only minor roles in the Ne-Ar cluster behavior, which was surprising considering the dominant role played by the Ar-core icosahedral-like isomers in the Ar-Kr clusters' behavior. So, for sake of comparison, I determined the icosahedral-like isomers for each Ne-Ar cluster by generating all the possible permutations from an icosahedral structure, and then minimized each one using the quench

routines, as described above.

III. RESULTS AND DISCUSSION

The structural and thermodynamics results obtained for 13-atom Ne-Ar clusters were very much different than those obtained for their Ar-Kr counterparts.[1] The small difference between the Ar and Kr atom sizes led to the Ar-Kr clusters essentially having topological configurations that were very similar to their homogeneous counterparts, but with many additional permutational isomers arising from the different arrangements of the Ar and Kr atoms within each type of topological form. As a consequence, the behavior of 13-atom Ar-Kr clusters was mostly similar to that of their homogeneous counterpart, and each cluster in the series still retained the characteristic magic number behavior. Like the Ar_{13} heat capacity curve, the Ar-Kr heat capacity curves were dominated by a huge peak in the solid-liquid transition region. Variations within the series arose primarily because of the energy differences between the permutational icosahedral-like isomers having an Ar atom core and the icosahedral-like isomers having a Kr core. For each cluster, the lowest energy isomer corresponded to a segregated Ar-core icosahedral-like isomer, with the other more mixed Ar-core icosahedral-like permutational isomers having only slightly higher energies. These closely spaced isomers gave rise to a very small, low-temperature peak in the heat capacity for those clusters having more than one such isomer. The Kr-core icosahedral-like permutational isomers' energies likewise formed a narrow group. The energy gap between the two sets of permutational isomers was very large for $Ar_{12}Kr$, but decreased markedly across the series as the number of Kr atoms increased. This resulted in initially small changes in the low-temperature side of the solid-liquid transition region heat capacity peak that grew to eventually form an additional, smaller heat capacity peak for $ArKr_{12}$. For 13-atom Ne-Ar clusters though, the large size difference between the Ne and Ar atoms ($\sigma_{\text{Ar-Ar}}/\sigma_{\text{Ne-Ne}} = 1.239$ compared to $\sigma_{\text{Kr-Kr}}/\sigma_{\text{Ar-Ar}} = 1.062$) resulted in many new non-icosahedral topological forms having no homogeneous counterparts. These dominated the solid-liquid transition region

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for many of the clusters, especially those consisting mostly of Ne atoms, drastically effecting their resultant heat capacity behavior.

A. Structural properties

It is those few isomers having the lowest energies that often dominate the solid-liquid transition region in small clusters. For example, quench studies of Ar_{13} have shown that at the solid-liquid transition region heat capacity peak temperature, the lowest 4 isomers accounted for about 80% of the quenched configurations.[1] Thus much insight can be obtained by examining a cluster's low-lying isomers and their energy distribution. Figure 2 shows the 13 lowest energy isomers found for each of the Ne-Ar clusters; their energies are listed in Table II. Unlike the low-lying isomers for Ar-Kr, which were all readily recognizable as variations of the 4 most stable 13-atom homogeneous cluster configurations, the low-lying Ne-Ar isomers are mostly non-icosahedral. The isomers depicted were all obtained from quenches of J-walker distribution configurations, except for the Ne-core icosahedral-like isomers for Ne_9Ar_4 (fifth lowest), Ne_7Ar_6 (second lowest), Ne_4Ar_9 (eighth lowest), and $NeAr_{12}$ (second lowest), which were not found in the quenched distributions and so were obtained instead by quenching the permutations derived from icosahedral structures. In fact, very few of the Ne-core icosahedral-like permutational isomers predicted by the icosahedral atom-counting rules[15] were found in the quenched J-walker distributions, unlike the case for 13-atom Ar-Kr clusters, where all of the expected permutational icosahedral-like isomers were found.

The lowest energy isomer found for $Ne_{12}Ar$ was icosahedral-like, consisting of a 12-atom Ne sub-cluster stacked on the Ar atom; the remaining isomers consisted of the small Ne atoms wrapped around the larger Ar core in various monolayer forms. Although the large difference between the Ne-Ar and the Ne-Ne potentials favors monolayer structures, the most efficient Ne packing is in the stacked structure, and in this case, the packing efficiency overshadowed the differential strengths of the potentials by a fairly large margin,

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with the difference between the stacked configuration and the lowest monolayer configuration being $1.31042\epsilon_{\text{Ne-Ne}}$. The stacked and monolayer forms are reminiscent of the wetting and nonwetting structures observed by Chartrand, Shelley and Le Roy[20] in their study of SF_6–(rare gas)$_n$ clusters. They observed both stacked (or nonwetted) and monolayer (wetted) structures for all the clusters $n \geq 4$ for SF_6-Ar_n and $n \geq 5$ for SF_6-Kr_n, with wetted isomers having the lowest energy for some n, and nonwetted isomers for the others. For $n = 12$, the ground state configuration for both Ar and Kr had the larger SF_6 located on the exterior of a stacked 12-atom sub-cluster, while in the second-lowest energy configuration, the SF_6 core was surrounded by a monolayer of rare gas atoms. For SF_6-Ar_{12}, the energy difference was $1.544\epsilon_{\text{Ar-Ar}}$, which is similar to the $Ne_{12}Ar$ energy difference in the analogous reduced units. Note also, that the size difference between the Ne and Ar atoms is similar to the size difference between Ar and SF_6. For the SF_6-Rg_n clusters, pentagonal and fused pentagonal caps were especially stable configurations that appeared often in the isomers for $n \geq 6$, and these are likewise evident in many of the $Ne_{12}Ar$ isomers shown in Fig. 2.

For $Ne_{11}Ar_2$, there are 3 Ne-core icosahedral-like structures possible. The lowest energy isomer found consisted of an icosahedral-like structure with the 2 Ne atoms occupying adjacent sites, analogous to the $Ar_{11}Kr_2$ lowest energy isomer. But unlike $Ar_{11}Kr_2$, there were also two non-icosahedral isomers having energies lower than the other two icosahedral-like permutational isomers. These non-icosahedral isomers are characterized by a 6-atom ring wrapped around the axis formed by the 2 Ar atoms. The other 5 Ne atoms occupied the various interstices formed by this Ne_6Ar_2 sub-cluster. The lowest energy non-icosahedral configuration had the 5 Ne atoms forming a partial second ring just beneath the 6-atom ring. This arrangement can also be seen to form two fused pentagonal caps, each consisting of one of the Ar atoms and 4 Ne atoms capped by a fifth Ne atom. This is a relatively stable configuration, so unlike the $Ne_{12}Ar$ case, the energy difference between the lowest energy stacked and monolayer configurations was very small ($0.0537\epsilon_{\text{Ne-Ne}}$).

The increase in the Ne-core icosahedral-like isomer energies relative to the non-icosahedral isomers continued for $Ne_{10}Ar_3$, which has 5 such isomers. The lowest energy

icosahedral-like isomer (analogous to the ground state $Ar_{10}Kr_3$ isomer) was not the ground state isomer, but ranked third lowest; the second-lowest Ne-core isomer ranked eleventh. Unlike the Ar-Kr clusters, the 5 Ne-core icosahedral-like isomers were not closely spaced in energy. Their energy range was $1.74461\epsilon_{Ne-Ne}$, compared to $0.12115\epsilon_{Ar-Ar}$ for the 5 analogous $Ar_{10}Kr_3$ Ar-core isomers. The non-icosahedral configurations shown in Fig. 2 each consist of the 3 Ar atoms arranged in a trigonal plane having 3 of the Ne atoms stacked on them in an opposing trigonal plane, and the remaining Ne atoms occupying various sites around them. The lowest energy configuration has C_{3v} symmetry.

The lowest energy isomer for Ne_9Ar_4 also consisted of the Ar atoms arranged in the lowest energy homogeneous sub-cluster configuration (the tetrahedron in this case), with the Ne atoms occupying the exterior sites. Its structure was very similar to the second lowest energy $Ne_{10}Ar_3$ isomer, with the main difference being the replacement of the Ne atom directly behind the 3 Ar atoms by another Ar atom. Similarly, the second lowest energy Ne_9Ar_4 isomer had a structure akin to the ground state structure of $Ne_{10}Ar_3$, with the main difference again being the replacement of the Ne atom directly behind the 3 Ar atoms by another Ar atom, so that the structure also has C_{3v} symmetry. The other Ne_9Ar_4 isomers can also be obtained formally from similar $Ne_{10}Ar_3$ structures by replacing a Ne atom with an Ar atom. Ne_9Ar_4 also has 10 Ne-core icosahedral-like isomers. The lowest energy one (analogous to the ground state Ar_9Kr_4 isomer) ranked fifth lowest. The second and fourth lowest energy Ne_9Ar_4 icosahedral-like isomers were found in the quench distribution, but none of the other 7 were. The reason for the absence of the Ne_9Ar_4 icosahedral-like isomers in the quenched distributions was evident in the quench trajectories obtained from one of the J-walking walks: almost all of the very few lowest energy Ne-core icosahedral-like isomers encountered during the walk quenched down to the global minimum, implying that the barriers to rearrangement between the two isomers are low. Thus, while the quenched J-walker distributions did not contain all of the low-lying isomers, the manner in which they were obtained suggests that they did contain the most important stable isomers, and that the shortfall consisted primarily of those isomers having low likelihood and being easily

rearranged. Again, the energy spread between the Ne_9Ar_4 Ne-core icosahedral-like isomers was very large ($2.34926\epsilon_{Ne-Ne}$ compared to $0.16439\epsilon_{Ar-Ar}$ for Ar_9Kr_4).

The lowest energy configuration for a 5-atom Lennard-Jones cluster is the trigonal bipyramid,[39] and so it not surprising that the lowest energy isomer for Ne_8Ar_5 consisted of the 5 Ar atoms arranged in a trigonal bipyramid configuration, with the 8 Ne atoms attached to the exterior sites, resulting in C_{2v} symmetry. The other low-lying non-icosahedral isomers had a similar form, with some of the Ne atoms occupying other exterior locations. The lowest energy configuration for a 6-atom Lennard-Jones cluster is the octahedron, but the tripyramid is only a little higher in energy (-12.30293ϵ compared to -12.71206ϵ) and the two are connected by low saddle points.[39] As can be seen in Fig. 2, the lowest energy non-icosahedral isomers found for Ne_7Ar_6 all have their 6 Ar atoms arranged in the tripyramid form, and not the lower energy octahedron. The lowest energy octahedral isomer, which has each Ne atom located on one of the octahedral faces, was the 36th lowest energy isomer found, with an energy of $1.63820\epsilon_{Ne-Ne}$ above the global minimum. Although the Ar-Ar interactions are maximized slightly in the octahedral arrangement, the Ne-Ne interactions are reduced substantially, making such configurations unfavorable. Ne_7Ar_6 has 18 Ne-core icosahedral-like isomers, and the lowest energy one ranked second; it was not found in the quenched distributions, and only two of the other 17 isomers were found. According to the icosahedral atom-counting rules,[15] Ne_7Ar_6 is also expected to have 12 Ar-core icosahedral-like isomers, but because the Ne atoms are too small to remain fixed in the icosahedral sites around the much larger Ar core atom, many additional isomers resembling highly distorted icosahedral-like forms are possible. Most of these were found in the quenched distributions. Their energies were generally higher than the Ne-core icosahedral-like isomer energies, but because of the large energy spread in both sets of isomers, there was substantial overlap. The lowest-energy Ar-core icosahedral-like isomer had an energy of $1.99495\epsilon_{Ne-Ne}$ relative to the global minimum.

The 7-atom Lennard-Jones cluster is one of the magic number sizes, having a pentagonal bipyramidal structure for its lowest energy isomer. Most of the Ne_6Ar_7 low energy isomers

shown in Fig. 2 consist of the 6 Ne atoms located on the trigonal faces of an Ar-atom pentagonal bipyramidal sub-cluster. The lowest energy isomer has 2 pairs of Ne atoms located on the upper trigonal faces, and the other pair located on the lower face below. The pentagonal sites formed by the Ar-atom ring are separated by distances much larger than the Ne-Ne equilibrium distance, and so the distances between the Ne atoms in each pair are compressed substantially. The second lowest energy isomer for Ne_6Ar_7 is readily recognizable as a truncated Ar-core icosahedral-like structure, with one of the Ne atoms located on one of the Ar icosahedral faces. If the Ne atom were moved to the top to cap the 5-atom Ne ring, the resulting configuration would be the lowest energy Ar-core icosahedral-like isomer. This isomer ranked 24th lowest, with an energy of $1.11047\epsilon_{\text{Ne-Ne}}$ above the ground state. The energy gained by increasing the number of Ne-Ar interactions in the truncated icosahedral-like form is much greater than the energy lost by breaking the compact icosahedral structure. The third lowest energy isomer did not have its Ar atoms arranged as a trigonal bipyramid, but as an incomplete stellated tetrahedron, the second lowest 7-atom Lennard-Jones isomer.[39]

Ne_5Ar_8 represents an interesting cross-over point in the 13-atom Ne-Ar series. It is the last in the series having a non-icosahedral structure as its lowest energy isomer — Ne_4Ar_9 to $NeAr_{12}$ all have Ar-core icosahedral-like isomers as their ground state isomers. Thus, it is also the last in the series to have its lowest energy Ne-core icosahedral-like isomer being more stable than its lowest energy Ar-core icosahedral-like isomer. The lowest energy isomer consists of the 8 Ar atoms arranged as a fully stellated tetrahedron, with the 5 Ne atoms located on the tetrahedral faces. The stellated tetrahedron is the second lowest energy isomer for 8-atom homogeneous Lennard-Jones clusters (the pentagonal bipyramid with an added atom is the lowest energy isomer).[39] The energy difference between the two is not small (-19.82149ϵ compared to -18.97606ϵ), but the larger number of Ne-Ar nearest neighbor interactions in this conformation is sufficient to overcome the deficit. Except for the third lowest energy isomer, which is a Ne-core icosahedral-like structure, all the other Ne_5Ar_8 isomers depicted in Fig. 2 consist of the Ar atoms arranged in the lowest energy

8-atom homogeneous sub-cluster. The second lowest energy isomer is a truncated Ar-core icosahedral-like structure, having one of the Ne atoms occupying one of the icosahedral faces formed by 3 Ar atoms. This structure is only slightly more stable than the lowest energy Ar-core icosahedral-like isomer, which ranked tenth lowest, but only $0.12235\epsilon_{\text{Ne-Ne}}$ higher in energy.

For Ne_4Ar_9, the two lowest energy isomers were Ar-core icosahedral-like permutational isomers, and so this cluster was the first in the series to have Ar-core icosahedral-like isomers that were lower in energy than their corresponding truncated icosahedral-like isomers. The energy ranges of the icosahedral-like and truncated icosahedral-like permutational isomers were both larger than the energy difference between the two sets, and so the isomers were mostly interspersed. As the number of Ar atoms increased, so too did the energy difference between the two sets, and they became increasingly segregated. For $\text{Ne}_3\text{Ar}_{10}$, the 4 lowest energy isomers were Ar-core icosahedral-like permutational isomers, and the fifth one ranked twelfth lowest overall. For $\text{Ne}_2\text{Ar}_{11}$, all 3 Ar-core icosahedral-like permutational isomers lay well below the truncated icosahedral-like permutational isomers, and the lone Ne-core icosahedral-like isomer was fourth lowest. For NeAr_{12}, the Ar-core icosahedral-like isomer lay well below its Ne-core counterpart. This energy was similar to the energies of the next three truncated icosahedral-like isomers, all of which have the Ne atom occupying one of the exterior sites. The subsequent isomers were also separated from these isomers by nearly as large an energy gap.

The trends in the lowest energy icosahedral-like and non-icosahedral isomers as functions of the cluster composition can be seen in Fig. 3. The reduced energies show a nearly linear dependence on composition that is due to the large difference between the Ne and Ar intermolecular forces. As the fraction of Ar atoms increased, so too did the fraction of stronger Ar-Ne and Ar-Ar interactions. This effect overshadowed the smaller, more subtle trends, which can be made manifest by scaling out the gross linear dependence on composition by using energies scaled by the composition weighted average $\epsilon_{\text{Avg}} = X_{\text{Ne}}\epsilon_{\text{Ne-Ne}} + X_{\text{Ar}}\epsilon_{\text{Ar-Ar}}$, where $X_{\text{Ne}} = n_{\text{Ne}}/(n_{\text{Ne}} + n_{\text{Ar}})$ and $X_{\text{Ar}} = 1 - X_{\text{Ne}}$. The icosahedral-like isomers' scaled en-

ergies increased as their mole fraction decreased from unity. For the Ne-core isomers, they rose rapidly from Ne_{13} until they leveled off at Ne_9Ar_4, and then decreased slightly again after Ne_6Ar_7. The Ar-core scaled energies likewise increased from the Ar_{13} value as the number of Ne atoms increased. However, they did not level off, but kept rising in a roughly linear manner. The two Ne-Ar icosahedral-like curves crossed at Ne_5Ar_8. These trends are strongly dependent on the atomic sizes, though. Had the Ne and Ar atoms been the same size, then the Ar-core isomers would have been more stable than the Ne-core isomers for all compositions, since the central Ar atom would have maximized the Ne-Ar interactions relative to the weaker Ne-Ne interactions. For 13-atom Ar-Kr clusters, the size difference between the Ar and Kr atoms was sufficiently large that the trends reversed and the Kr-core isomers were higher in energy than the Ar-core isomers for all compositions. The Ne-Ar curves demonstrate that there exists another critical size ratio for those icosahedral-like isomers consisting mostly of the larger-atom component, where having the larger atom at the center becomes more stable again than having the smaller atom at the center. The scaled energies for the non-icosahedral isomers were roughly constant across the series. The similarity of the scaled energies for these isomers indicates that these clusters had non-icosahedral ground state structures not because the isomers themselves became intrinsically more stable as the composition became more mixed, but because the icosahedral-like isomers became so much less stable.

The effects of cluster composition on the isomer energy distributions are shown in Fig. 4, which depicts the energy spectrum for each cluster's local minima relative to its global minimum. The plots have been arranged so that complementary clusters ($Ne_{13-n}Ar_n$ and Ne_nAr_{13-n}) appear in the same column. As was the case with 13-atom Ar-Kr clusters, the densities of the energetically distinct local minima increased as the number of possible permutations increased, quickly becoming so great that most of the individual levels cannot be distinguished in the plots. Otherwise, though, the plots differ greatly from the Ar-Kr plots. In those plots, the clusters having a greater fraction of Ar atoms had an energy spectrum similar to that of Ar_{13}, which is dominated by its very large energy gap between the icosa-

hedral ground state and the non-icosahedral isomers. As the fraction of Kr atoms in the clusters increased from $Ar_{12}Kr$ to Ar_7Kr_6, the number of Ar-core icosahedral-like permutational isomers increased, forming a small group of closely spaced low-lying energies, but the energy gap between these isomers and the band formed by the higher energy truncated icosahedral and non-icosahedral isomers remained nearly constant. The Kr-core icosahedral-like isomers were also closely spaced, but the gap between them and the Ar-core isomers decreased steadily as the Kr mole fraction increased. The Ne-Ar energy spectra do not exhibit such patterns, showing instead, a wide variety of behavior. Except for $NeAr_{12}$, none of the binary cluster spectra has the large gap between the global minimum and the higher energy isomers that characterize the homogeneous cluster spectra. The number of low lying isomers ($\Delta E \lesssim 2$) is greater for those clusters having similar numbers of Ne and Ar atoms, being greatest for Ne_5Ar_8. For these clusters, the low-lying icosahedral-like and non-icosahedral isomers have similar energies so that the two sets are substantially interlaced.

B. Thermodynamic properties

The wide variety that characterizes the structural properties of 13-atom Ne-Ar clusters carries over to their thermodynamic properties as well. Figure 5 shows the heat capacity (in reduced units) for each cluster as a function of temperature. The heat capacity peak heights and temperatures are listed in Table III, and the values for the major peaks are plotted in Fig. 6. The J-walking curves shown in each plot in Fig. 5 represent the averages obtained from combining the results of the individual J-walking runs, as described in Section II. Representative standard deviations have not been included to prevent excessive cluttering, but they were consistent with the noise levels evident in the curves. The peak values were obtained in each case from the averaged J-walker curves. These curves were smoothed and then interpolated in the peak vicinities to obtain finer mesh sizes, and the peak parameters were then found simply by searching the interpolated data.[40] The uncertainties in the peak heights were estimated from the average standard deviations of the points in the vicinity of

each peak.

The plots of the Ne-Ar heat capacity peak temperature and height as functions of composition shown in Fig. 6 do not exhibit the smooth variations that were seen in the corresponding plots of their Ar-Kr counterparts. The Ne-Ar peak temperatures can be grouped into three regions: Ne_{13} to $Ne_{10}Ar_3$, which have similar, but much lower peak temperatures than the others; Ne_9Ar_4 to Ne_4Ar_9, whose peak temperatures are roughly constant; and Ne_3Ar_{10} to Ar_{13}, whose peak temperatures rise nearly linearly as a function of the composition. The linear rise in the peak temperature is similar to the trends observed for the Ar-Kr clusters, which showed a gradual linear rise from Ar_{13} to Ar_7Kr_6, followed by a steeper linear rise from Ar_6Kr_7 to Kr_{13}. The changes in the Ar-Kr peak heights were relatively minor, with the difference between the maximum and minimum being only about 12% of the Ar_{13} peak height. The changes in the Ne-Ar peak heights were much more drastic. Again, it was those Ne-Ar clusters having a large Ar mole fraction whose behavior most resembled that of their Ar-Kr counterparts. Also shown in Fig. 6 is a plot of the peak heights as a function of the peak temperature. Unlike the corresponding plot for the Ar-Kr clusters, though, which consisted of a regular progression on a smoothly varying curve, the Ne-Ar plot consists of an irregular scatter of points with some grouping evident.

Except for the $NeAr_{12}$ heat capacity curve, none of the curves shown in Fig. 5 resembles the Ar_{13} curve obtained previously,[2,6] unlike the Ar-Kr curves, which were mostly very similar to the Ar_{13} curve in the solid-liquid transition region. The similarity in the Ar-Kr curves was a consequence of the Ar-core icosahedral-like permutational isomer energies being closely spaced and well separated from the Kr-core icosahedral-like energies, and from the non-icosahedral energies, so that the important differences occurred only in the low temperature regions. Except for $NeAr_{12}$, the Ne-core icosahedral-like, Ar-core icosahedral-like, and the non-icosahedral isomer energies were not well separated, but were mostly intermixed, so that there were few large gaps in the energy spectra. This resulted in the much diminished heat capacity peaks evident in Fig. 5.

The standard Metropolis heat capacity curves for each cluster have also been included

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in Fig. 5. These were in good agreement with the J-walking curves over most of the temperature domain for only a few of the clusters, but were in mostly good agreement with all of them at the higher temperatures. The poor results obtained from the standard Metropolis method in the low temperature regions was not surprising since this was evident in the 13-atom Ar-Kr Metropolis results as well, where the low temperature mixing-anomaly peaks were not reproduced at all. What was surprising is how little improvement was obtained using the atom-exchange method. For the Ar-Kr clusters, the atom-exchange results were substantially better than the standard Metropolis results, and were in good agreement with the J-walker results for all the clusters over most of their temperature domains. The atom-exchange results even showed the mixing-anomaly peaks, although they were only in qualitative agreement with the J-walker results. As is evident in Fig. 5, the atom-exchange results were mostly similar to the standard Metropolis results for most of the Ne-Ar clusters. The poor performance of the atom-exchange method in application to Ne-Ar clusters is also due to the large size difference between the Ne and Ar atoms. In the low temperature regions where most of the Metropolis configurations have energies only slightly above their nearest local minimum, the trial configurations most often obtained by swapping one of the large Ar atoms with a small Ne atom were strained configurations having energies too high to be accepted with sufficient frequency. Comparison of the exchange-move acceptance ratios for the Ne-Ar clusters with the ratios for their corresponding Ar-Kr counterparts showed that indeed far fewer exchange moves had been accepted for the Ne-Ar clusters. It appears then, that the atom-exchange method is useful for reducing quasiergodicity in binary cluster simulations only when the atomic sizes of the two components are similar enough.

Much of the low temperature Ne-Ar heat capacity behavior seen in Fig. 5 can still be rationalized mainly in terms of the potential minima energy spectra shown in Fig. 4, although there are other important factors involved as well. The curves for the predominately Ne clusters $Ne_{12}Ar$, $Ne_{11}Ar_2$ and $Ne_{10}Ar_3$ differed from the others by their much lower peak temperatures, and by their much smaller peak sizes. The peak temperatures were all substantially below the Ne_{13} peak temperature of 10.15 K. $Ne_{12}Ar$ had a single moderately

high peak occurring at 5.20 K that was evident only in the J-walking calculations; the Metropolis and atom-exchange results showed an abrupt rise in the heat capacity at 6 K, but no peak. The peak is due to the moderately large energy gap between the stacked ground state icosahedral-like isomer and the Ar-core monolayer isomers. The rest of the curve rising sharply after the peak is the low temperature side of a larger peak associated with the cluster's dissociation.[41] It is tempting to extend the correspondence between the Ne_{13} heat capacity peak and its solid-liquid transition region to $Ne_{12}Ar$ and to think of its peak then as characterizing a solid-liquid transition between the "solid" stacked configuration and the "liquid" monolayer configurations, but this is not the case. The absence of a peak in the Metropolis results implies that this peak is not due to any dynamic transition between the stacked and monolayer isomers, and so cannot represent a coexistence region like the one in Ne_{13}. Instead, once the Metropolis simulations reached 6 K, the $Ne_{12}Ar$ clusters began achieving energies high enough to overcome the potential barriers separating the stacked configurations from the other low-lying isomers, whereupon they escaped their confinement, transformed into one of the monolayer configurations and were seldom encountered again. As will be discussed later, the quench studies revealed that as the temperature continued increasing, it was the monolayer isomers that dominated the solid-liquid transition region, which occurred at higher temperatures.

For $Ne_{11}Ar_2$, the Ne-core icosahedral-like ground state and the lowest energy non-icosahedral isomer have very similar energies, which resulted in the very small heat capacity peak occurring at 0.37 K. As with $Ne_{12}Ar$, there was a very large discrepancy between the J-walking and Metropolis results over much of the low temperature region. The Metropolis curve rose slowly and nearly linearly until about 6 K, after which it rose abruptly to approach the J-walking curve. The curves form a larger peak at 8.92 K that can be identified, in conjunction with the quench studies discussed later, as the solid-liquid transition region. $Ne_{10}Ar_3$ had a peak that was more pronounced than the peak for $Ne_{11}Ar_2$, and it was located at a slightly lower temperature of 6.76 K. The Metropolis and atom-exchange curves for $Ne_{10}Ar_3$ were in much better agreement with the J-walking curve than was the

case for the other two clusters. Although the Metropolis peak was much diminished and the curve on the low temperature side of the peak was much lower than the J-walking curve, the results were at least in qualitative agreement.

The predominately Ar clusters Ne_3Ar_{10} to $NeAr_{12}$ were distinguished by a single large peak corresponding to the solid-liquid transition region. The peaks became smaller and shifted to lower temperatures as the number of Ar atoms decreased. Their larger size is due to the very large gaps between the lowest energy isomers and the band of higher energy isomers that are accessible only at the higher temperatures associated with the liquid region. As the gap decreased from Ar_{13} to Ne_3Ar_{10}, so too did the peak height. These clusters also have sufficiently large energy gaps between the ground state isomer and the next lowest energy isomer that none exhibited the small, very low temperature heat capacity peaks seen in some of the other clusters. While the heat capacity curve for $NeAr_{12}$ most resembled the Ar_{13} curve, it differed much from its $ArKr_{12}$ counterpart. The $ArKr_{12}$ curve had a smaller, well separated second peak occurring just before the solid-liquid transition peak that was due to the interaction between the Ar-core and Kr-core icosahedral-like isomers. The isomer energy spectra for $NeAr_{12}$ and $ArKr_{12}$ are mostly similar. For $ArKr_{12}$, the Kr-core isomer having the larger Kr atom at the center was $3.15883\epsilon_{\text{Ne-Ne}}$ higher in energy than the Ar-core isomer. For $NeAr_{12}$, the energy gap between the Ne-core and Ar-core icosahedral-like isomers was only slightly larger ($3.99438\epsilon_{\text{Ne-Ne}}$), but in this case, it was the Ar-core isomer with its larger Ar atom at the center that had the lower energy. $NeAr_{12}$ also differs from $ArKr_{12}$ in that its 3 truncated icosahedral-like isomers with the Ne atom located on one of the icosahedral faces had energies only slightly higher than the Ne-core icosahedral-like isomer; in $ArKr_{12}$, the corresponding truncated icosahedral-like isomers had much higher energies, with the gap being similar to the one in Kr_{13}. Otherwise though, the two energy spectra differed little. This major difference between the $NeAr_{12}$ and $ArKr_{12}$ heat capacity curves despite their similar energy spectra clearly indicates that much more than just the isomer energy distributions are involved in the clusters' thermodynamic behavior. Both $NeAr_{12}$ and Ne_2Ar_{11} showed mostly good agreement between the J-walking and Metropolis

curves, while Ne_3Ar_{10} showed significant deviations on the low temperature side of the peak. For Ne_3Ar_{10}, the atom-exchange results were markedly better than the Metropolis results, though.

The heat capacities for the intermediate clusters Ne_9Ar_4 to Ne_4Ar_9 are characterized by very broad, low peaks extending over much of the temperature domain. While the curve profiles transformed smoothly in going from Ne_4Ar_9 to Ne_3Ar_{10}, there was an abrupt change in going from $Ne_{10}Ar_3$ to Ne_9Ar_4. The peaks for Ne_9Ar_4 to Ne_4Ar_9 occurred at much higher temperatures than did the peaks for $Ne_{12}Ar$ to $Ne_{10}Ar_3$, but their temperatures were similar to the solid-liquid transition peak temperatures obtained for Ne_3Ar_{10} to $NeAr_{12}$. While the similar peak temperatures might suggest that these peaks also corresponded to solid-liquid transitions, the peaks' broad profiles, extending over such large temperature ranges, together with the abrupt changes in the peak height and location between $Ne_{10}Ar_3$ and Ne_9Ar_4, indicates a more complicated scenario, one which will await the discussion of the quench results. Except for Ne_4Ar_9, the peak temperatures for this group were remarkably similar. The peak heights mostly decreased over this range as the Ar mole fraction increased, reaching a minimum at Ne_5Ar_8. Those clusters having isomers with energies slightly above their global minimum energy (Ne_9Ar_4, Ne_8Ar_5, Ne_6Ar_7, and Ne_5Ar_8) also had an additional small peak occurring at very low temperatures. In the Ar-Kr clusters, these smaller peaks' sizes were primarily determined by the number of Ar-core icosahedral-like isomers, since these isomers were grouped closely together in energy. For the Ne-Ar clusters though, the large spread of the various permutational isomer energy ranges implies that there is no such simple connection between the low-lying isomers and the size of the low temperature peaks: Ne_9Ar_4 had the largest such peak, which is due to the transactions between its lowest 3 non-icosahedral permutational isomers, while Ne_8Ar_5, with 5 low-lying non-icosahedral isomers, had a much smaller peak.

The potential energy curves for the clusters as functions of temperature are shown in Fig. 7. The large difference between the Ne and Ar intermolecular potentials results in the binary cluster curves having widely varying energies and temperature ranges, which makes

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it difficult to compare them directly. It is clear, though, that they differ qualitatively from the homogeneous cluster curves; except for the $Ne_{12}Ar$ and $NeAr_{12}$ curves, the curves for the binary clusters show very gradual rises occurring over more extended temperature ranges. The $Ne_{12}Ar$ curve has a noticeable inflection, but it occurs at a reduced temperature well below that of the Ne_{13} inflection.

C. Quench results

Further insights into the temperature dependence of binary cluster isomerizations can be obtained from the quench studies. Figures 8 to 10 show the quench results obtained using J-walking for the six lowest-energy isomers for each Ne-Ar cluster. Not surprising, the quench curves also show much variation, and are generally dissimilar from the corresponding homogenous cluster quench curves. This again is very much different than what occurred for the 13-atom Ar-Kr clusters, whose quench curves showed large differences due to the low-lying Ar-core icosahedral-like permutational isomers; if those curves were combined into single curves representative of their common icosahedral-like topological forms, then the resulting quench profiles were in fact very similar to their homogeneous counterparts.

For $Ne_{12}Ar$, the fraction of quenches to the ground state Ne-core icosahedral-like isomer dropped off rapidly after 4 K as the Ar-core monolayer isomers began to contribute, so that by 8 K, there were very few quenches to this isomer. The two lowest-energy monolayer isomers dominated the quenches over much of the rest of the temperature domain depicted, contributing about 75% of the quenches at 7 K (which the Metropolis heat capacity results indicate as being in the solid-liquid transition region), and about 40% of the quenches at 13 K, where the large fraction of quenches to the other higher energy isomers is indicative of liquid-like behavior. The curve for the remaining higher energy isomers rose much more slowly than was the case for the other predominately Ne clusters, implying that the solid-liquid transition region for $Ne_{12}Ar$ seems to extend over a much larger temperature range. Note too, that this curve becomes dominant well beyond the heat capacity peak,

again consistent with the Metropolis heat capacity behavior indicating that the solid-liquid transition region occurred at higher temperatures.

To gain more insight into the melting behavior of this cluster, I ran additional quench studies using similar Metropolis temperature scans in the direction of decreasing temperatures, starting at 10 K. Figure 11 compares the quench profiles obtained for the three lowest energy isomers from these simulations with those obtained from the Metropolis simulations in the direction of increasing temperatures, which were begun from the ground state isomer. The curves show clear hysteresis. The quench curves in the increasing temperature direction reveal that the clusters were locked into their lowest energy configuration until 6.3 K, after which the monolayer isomers began being accessed (this temperature also corresponds to the point where the Metropolis heat capacity curve rose abruptly in Fig. 5). Reversing the temperature direction at 10 K resulted in curves that were in agreement only for temperatures higher than 6.3 K, below which, none of the quenches were to the ground state isomer, but were distributed among the low lying monolayer isomers. This behavior implies that the barriers to isomerization between the monolayer configurations are very low, while the barriers between the stacked and the monolayer configurations are very large.

The spikes seen in the Metropolis quench curves near 7 K imply that this is a narrow coexistence region where the cluster spent long periods of time in either the stacked or monolayer configurations, switching between the two only occasionally. But this coexistence is quite different than the one occurring in Ne_{13}. For Ne_{13}, the coexistence region primarily involved isomerizations between the ground state icosahedron and the three higher energy truncated icosahedral structures having one of the atoms located on one of the icosahedral faces (at the heat capacity peak temperature, about 80% of the quenches were to these four isomers). It is the very large energy gap between the Ne_{13} ground state and the truncated icosahedral isomers, as well as the substantial gap between those isomers and the succeeding non-icosahedral isomers, that is responsible for the pronounced coexistence range in Ne_{13}. The gap between the $Ne_{12}Ar$ ground state and the corresponding truncated icosahedral-like isomers having a lone Ne atom on one of the icosahedral faces is slightly smaller than the

one in Ne_{13}, but as can be seen in Fig. 4, $Ne_{12}Ar$ has a large number of monolayer isomers with energies well below the truncated icosahedral-like isomers. Thus once a stacked $Ne_{12}Ar$ isomer at about 6.3 K gained sufficient energy to move a Ne atom from an icosahedral vertex onto an icosahedral face, it reached a plateau region where the lone Ne atom could return again to its icosahedral site, or the cluster could continue isomerizing into one of the monolayer isomers. But once it started down the monolayer path, it could easily continue isomerizing into several of the various monolayer isomers, since the barriers separating them are so low. Such a trajectory would cover a much larger distance in configuration space, greatly reducing the likelihood of its return to the original stacked configuration. For Ne_{13}, the four lowest energy isomers are close together in configuration space so that the isomerizations between them are largely reversible, and the typical recurrence times between isomers returning to icosahedral configurations are short on the time scale of the walk length. For $Ne_{12}Ar$, the recurrence times were so much longer that the transformations from stacked to monolayer configurations were largely irreversible, except for a very narrow temperature range, where the probability of crossing the barriers was so low that such an occasional transformation would leave the cluster trapped in the stacked configuration subspace for a long period of time before accessing enough energy to take it out again.

The icosahedral-like configuration subspace being so much smaller than the non-icosahedral configuration subspace, and it being isolated by large barriers, were also factors in the quench distributions for the other Ne-Ar clusters, where the quenches to Ne-core icosahedral-like isomers were also very low; it also accounts for the absence of many of these permutational isomers in the J-walker distributions noted earlier. Similar behavior was encountered by Matro, Freeman and Topper in their study of ammonium chloride clusters.[26] The second and third lowest energy isomers for $(NH_4Cl)_3$ were only slightly higher in energy than the lowest energy isomer ($\Delta E_{01} = 235$ K, $\Delta E_{02} = 635$ K) and separated from it by large barriers of nearly equal size ($\Delta E_{01} = 2118$ K, $\Delta E_{02} = 2021$ K). During the simulations at 50 K, all the configurations were found to be in the potential energy wells belonging to the first and third isomers, but none were found in the well belonging to the second isomer,

which the authors attributed to the much smaller fraction of configuration space associated with the second isomer.

Visually examining samples of the $Ne_{12}Ar$ configurations generated during Metropolis walks at various temperatures provided further support for the above arguments. Walks begun from an initial ground state configuration at 8 K quickly resulted in configurations that were distended, but quite recognizable as stacked Ne-core icosahedral-like structures. After a several thousand passes, the cluster isomerized into one of the truncated icosahedral-like forms, where the lone exterior Ne atom slowly migrated over the surface, moving from site to site, sometimes returning to its original site. Eventually, after many additional steps, the exterior Ar atom and the core Ne atom would make a concerted movement that brought the Ar atom into the central location and moved the central Ne atom to the exterior, transforming the cluster into an Ar-core precursor that quickly collapsed into a monolayer structure, after which the exterior Ne atoms rapidly rearranged themselves into various other monolayer configurations. The migration of exterior Ne atoms from one side of the Ar atom to another was still sluggish, though, because the Ne atoms enveloped the Ar atom closely enough to hinder gross movements. Repeating the walks at higher temperatures led to similar behavior, but on an accelerated time scale such that the transformation from stacked to monolayer configuration occurred much more quickly. The monolayer configurations also underwent isomerizations more rapidly as the exterior Ne atoms moved freely about the Ar core, showing large-scale movements akin to liquid-like behavior. The intermediate, partially stacked configurations were also seen more frequently. At the higher temperatures, the clusters often had enough energy to overcome the barriers between the monolayer and stacked configuration spaces, but because the stacked configuration subspace is so much smaller than the monolayer configuration subspace, only a small fraction of the walk was spent in the stacked subspace, resulting in few stacked configuration quenches. But for temperatures near 7 K though, the movement between the regions slowed down enough that the occasional forays into the stacked configuration subspace resulted in the Metropolis walker being trapped for long periods before escaping. Coexistence was not seen at lower

temperatures since the movements into the stacked subspace became so infrequent that the walker remained essentially trapped in the monolayer subspace.

This type of coexistence behavior between the stacked and monolayer configurations is also similar to the behavior reported by Shelley, Le Roy and Amar in their molecular dynamics study of SF_6-Ar_9 clusters.[19] The authors observed that the cluster underwent two different "melting" transitions, the first at $T \approx 15$ K marking the onset of Ar atom mobility within the unimolecular layer surrounding the SF_6 core, and the second at $T \approx 35$ K marking the onset of facile Ar atom motion out of and back into this layer. Over a narrow intermediate temperature range, the authors noted the coexistence between the "liquid-like" monolayer rearrangments and the solid-like large-amplitude motion of the stacked two-layer configurations. One of the fundamental differences between this coexistence and that seen for homogeneous Ar clusters was that the transition from the liquid-like monolayer isomers to the solid-like stacked isomers required an increase in energy; that is, the "solid" was obtained after heating the "liquid." This spontaneous reversing isomerization is analogous to the $Ne_{12}Ar$ behavior, since the large spikes in the Metropolis stacked isomer quench curves, as well as the small, but nonzero, values afterward, occurred at higher temperatures ($T \gtrsim 7$ K) than the temperature where the cluster first isomerized to the monolayer form ($T = 6.4$ K), and had no quenches to the stacked configuration at all.

The quench profiles for Ne_9Ar_4 and $Ne_{10}Ar_3$ show that much care must be exercised in interpreting quench results. Both clusters have similar profiles, differing mostly in the Ne_9Ar_4 curves showing abrupt changes about 2 K sooner, but whereas the $Ne_{10}Ar_3$ quench profile was consistent with the J-walking and Metropolis heat capacity results, the Ne_9Ar_4 profile was not. Ne_9Ar_4 has a much larger number of low-lying non-icosahedral isomers lying within $1\epsilon_{Ne-Ne}$ of the lowest energy isomer than does $Ne_{10}Ar_3$, but the high density of isomers above $1\epsilon_{Ne-Ne}$ from the global minimum is similar in both clusters. The curve representing the sum of the quenches to the higher energy isomers rises even more quickly in Ne_9Ar_4 because of the contributions from the many isomers lying within $1\epsilon_{Ne-Ne}$ of the ground state, suggesting that the temperature region near 4 K be interpreted as a solid-liquid transition

region as well. The heat capacity results, though, were more akin to those obtained for $Ne_{12}Ar$ than to those obtained for $Ne_{10}Ar_3$ — the Ne_9Ar_4 heat capacity peak was also seen only in the J-walking results. The Metropolis results showed a small rise in this region, but no discernible peak, again implying that these higher energy isomers were not accessed dynamically at these low temperatures, and so this region is not the solid-liquid transition region. The Ne_9Ar_4 heat capacity curve has another peak at 24.27 K having no counterpart in $Ne_{10}Ar_3$ that could be identified as the solid-liquid transition peak, but it seems surprising that replacing a single Ne atom with an Ar atom in $Ne_{10}Ar_3$ to form Ne_9Ar_4 could shift the transition temperature from 7 K to 24 K. Moreover, the peak is so broad that it is hard to imagine that it could represent a solid-liquid transition spanning a range from 5 to 30 K.

Visually examining samples of the Ne_9Ar_4 configurations generated during some of the Metropolis walks revealed that peak encompassed more than just a solid-liquid transition. At 5 K, the cluster showed only solid-like behavior for tens of thousands of passes, but at temperatures near 7 K, the Ar atoms remained fixed as a solid-like tetrahedral sub-cluster undergoing small amplitude oscillations, while a Ne atom occasionally moved from one site to another. Although there are many low-lying non-icosahedral isomers having similar energies, the barriers were too high for the Metropolis walks to overcome at such low temperatures; the ergodic J-walking could cover such large regions of configuration space, though, resulting in quenches to a wide distribution of isomers, but with relatively few to any one. Thus the quench profile appears similar to that of a cluster in the liquid region, even though none of the atoms were undergoing the rapid large scale movements characteristic of liquid-like behavior. As the Metropolis walk temperature was increased, the Ne atoms underwent increasingly large amplitude motions, eventually moving freely about the still solid-like Ar core. Much higher temperatures were required before the Ar atoms also started undergoing large amplitude motions and rearrangements from their tetrahedral sites. This implies that Ne_9Ar_4 underwent differentiated melting, with the outer Ne atoms "melting" well before the Ar core. At temperatures near the heat capacity peak, the Ne_9Ar_4 clusters showed full liquid-like behavior, but the Ne atoms would sometimes move quite far apart

from one another, and from the Ar atoms, which still tended to remain together, leading to dissociated configurations that would collapse again into condensed configurations after a short while.

The similar broad shapes of the heat capacity peaks for the other clusters up to Ne_3Ar_{10}, as well as their similar peak temperatures, indicate behavior similar to that of Ne_9Ar_4, with the peaks encompassing "pre-melting" isomerizations at low temperatures (evident where the J-walking and Metropolis curves showed larger discrepancies), "melting" of the outer Ne atoms (that is, free movement of the Ne atoms around an intact Ar sub-cluster core), melting of the Ar-core to give a fully liquid-like cluster (although with the Ne and Ar atoms more segregated than not), and dissociation of the Ne atoms (which remained about the undissociated Ar atoms because of the confining potential); full dissociation of the cluster was evident in other peaks occurring at slightly higher temperatures than shown in Fig. 5. None of these "stages" had sharply defined temperature ranges, but formed a continuum of behavior. As the number of Ar atoms increased, though, these stages shifted to higher temperatures and became increasingly differentiated, so that by Ne_4Ar_9, liquid-like behavior dominated the heat capacity peak region.

The lowest energy isomers for the predominately Ar clusters Ne_4Ar_9 to $NeAr_{12}$ were all Ar-core icosahedral-like structures having increasingly larger gaps between them and their next highest energy isomers. This is reflected in their quench profiles, shown in Fig. 10. The temperature at which the fraction of quenches to the ground state isomers began to drop increased as the number of Ar atoms increased. Ne_2Ar_{11} has its two other Ar-core icosahedral-like permutational isomers having similar energies at about $1\epsilon_{Ne\text{-}Ne}$ from the ground state. Their quench curves show that they too began being accessed by about 5 K, but while the second lowest energy isomer went on to contribute a maximum of 20% of the quenches at 18 K, the third isomer had very few quenches throughout. This behavior is similar to that observed for Ar-Kr clusters, where the different quench levels for icosahedral-like permutational isomers was due primarily to simple combinatorics. As can be seen in Fig. 2, the third lowest-energy isomer has its two Ne atoms occupying the axial positions of

the icosahedron. The number of ways that the two Ne and 11 Ar atoms can be combined to form this arrangement is much smaller than the number of ways the other two permutational isomers can be formed. The fourth lowest energy Ne_2Ar_{11} isomer is a Ne-core icosahedral-like isomer, and like most of the other Ne-core icosahedral-like isomers for the other Ne-Ar clusters, it had very few quenches.

The quench profile for $NeAr_{12}$ is similar to that of Ar_{13}. $NeAr_{12}$ has a Ne-core icosahedral-like isomer, as well as three truncated Ar-core icosahedral-like isomers having the lone Ne atom located on one of the icosahedral faces. The Ne-core icosahedral-like isomer again had very few quenches, but the other three isomers began being accessed at about 20 K, reaching a maximum at the heat capacity peak temperature. These three isomers and the ground state isomer accounted for 75% of the quenches at the heat capacity peak temperature, which was similar to Ar_{13}, whose four lowest isomers accounted for 80% of the quenches at the heat capacity peak temperature. The quench profile for $NeAr_{12}$ is very much different than that of its $ArKr_{12}$ counterpart, though. Its analogous Kr-core icosahedral-like isomer also dominated the quenches near the heat capacity peak temperatures, but since this isomer was the higher energy one, it started with no quenches at the very low temperatures where the ground state Ar-core isomer was dominant. $ArKr_{12}$ had a moderately sized heat capacity peak occurring below the solid-liquid transition peak that corresponded to the transformation from the Ar-core to the Kr-core isomer. Because the analogous Ne-core isomer was not the ground state isomer for $NeAr_{12}$, there was no analogous transformation from it to the Ar-core isomer, and so there was no smaller heat capacity peak for $NeAr_{12}$ corresponding to the one for $ArKr_{12}$.

IV. CONCLUSION

The results obtained for 13-atom Ne-Ar clusters were very much different than those obtained for their Ar-Kr counterparts. Where the Ar-Kr cluster properties were mostly alike and similar to those of their homogeneous counterpart, the Ne-Ar cluster properties exhibited a wide range of diverse and unique behavior that showed little semblance to their

corresponding homogeneous cluster properties. For example, $Ne_{12}Ar$ and $Ne_{11}Ar_2$ clusters underwent transitions from stacked Ne-core icosahedral-like configurations to Ar-core mono-layer configurations that none of the other clusters did. Ne_4Ar_9 and Ne_3Ar_{10} were much alike, but their complements Ne_9Ar_4 and $Ne_{10}Ar_3$ were very different from one another. All the Ar-Kr clusters showed the magic-number behavior characteristic of Ar_{13}, but except for $NeAr_{12}$, none of the Ne-Ar clusters did. Analogous to Ar_{13}, whose icosahedral and much higher energy truncated icosahedral isomers dominated the solid-liquid transition region, the Ar-Kr clusters' solid-liquid transition regions were dominated by closely spaced Ar-core icosahedral-like permutational isomers and higher energy truncated icosahedral-like permu-tational isomers. For the Ne-Ar clusters, though, the corresponding Ne-core icosahedral-like and truncated icosahedral-like permutational isomers played important roles only for $Ne_{12}Ar$ and $Ne_{11}Ar_2$, and were conspicuously absent for the others. Instead, the low-lying Ne-Ar isomers were dominated by different types of non-icosahedral isomers, many of which had no homogeneous counterparts. The permutational isomers derived from the low-energy Ne-Ar topological forms did not have energies lying in closely spaced groups that were separated from one another by large gaps, as was the case for the Ar-Kr clusters. Instead, the Ne-Ar permutational isomer energies for the various topological forms were typically spread out over ranges that were comparable or larger than the differences between the different sets, leading to very interspersed isomer energy spectra; most of the Ne-Ar clusters were devoid of any large gaps in their minima energy spectra.

These large differences in behavior between the 13-atom Ne-Ar and Ar-Kr clusters result primarily from the disparateness between the Ne and Ar atomic sizes compared to the much more similar Ar and Kr sizes, and to a lesser extent, from the large difference between the Ne and Ar intermolecular forces compared to the Ar and Kr forces. The former primarily ef-fected the cluster packing efficiency, decreasing the extraordinary stability of the icosahedral structure to such an extent that the icosahedral-like isomers energies became comparable to the non-icosahedral isomer energies for most of the Ne-Ar clusters; this mostly effected the clusters' low-temperature behavior. The latter was predominant at higher temperatures

and resulted in extended solid-liquid transition regions. Ar-Kr clusters, like their homogeneous counterpart, underwent solid-liquid transitions over temperature ranges that, while not sharply delimited, could be nonetheless differentiated by the abrupt changes in many of their properties. The Ar and Kr atoms were similar enough that the modifications in the clusters' transition behavior were largely minor. For many of the Ne-Ar clusters, though, as the temperature increased from the solid region, the clusters underwent a pre-melting stage where the Ar atoms remained fixed as a solid sub-cluster core undergoing low amplitude motions, while the Ne atoms wrapped around the Ar core, slowly moving from site to site. Increasing the temperature led to liquid-like motion of the Ne atoms as they moved with little hindrance around the still solid-like Ar sub-cluster core. For those clusters having more than 4 Ar atoms, much higher temperatures were required before the Ar core also showed liquid-like behavior. At these temperatures, the atoms moved freely about one another, although the Ne and Ar atoms still tended to segregate, with the Ar atoms mostly in the center. Similarly, as the temperature increased from the liquid region, the Ne atoms dissociated first, resulting in a liquid-like Ar-atom sub-cluster surrounded by freely moving Ne atoms, confined within the constraining volume. These transitions each had extended temperature regions of several degrees that mostly overlapped, so that the overall solid-liquid transitions occurred over a much wider temperature range, resulting in very broad heat capacity peaks with peak heights that were mostly much lower than those obtained for the Ar-Kr clusters. As the number of Ne atoms diminished, the melting behavior transformed into the more usual differentiated behavior, so that by $NeAr_{12}$, the melting behavior was quite similar to that of Ar_{13}.

The results obtained for the Ne-Ar clusters again demonstrated the need to consider several cluster properties together, in context to one another, when attempting to interpret their underlying behavior. While the J-walking simulations were able to provide accurate heat capacities and quench profiles, these were insufficient in themselves to interpret the solid-liquid transition behavior. The J-walking results for $Ne_{12}Ar$ showed a pronounced heat capacity peak that seemed indicative of a solid-liquid transition, and the quench pro-

files were consistent with such an interpretation. However the Metropolis heat capacity and quench results, as well as visual inspections of the configurations obtained during Metropolis walks, indicated that the solid-liquid transition region occurred at higher temperatures. The $Ne_{12}Ar$ J-walking heat capacity peak was due to the increased fluctuations in the cluster's energies arising from the ergodic sampling of the stacked isomer's and monolayer isomers' configuration subspaces — the peak occurred at too low a temperature for dynamic motions to overcome the barriers between these regions, and so it was more akin to the low temperature mixing anomaly peaks observed in the Ar-Kr clusters than to their solid-liquid transition peaks. Similarly, the J-walker quench profiles for $Ne_{10}Ar_3$ and Ne_9Ar_4 were alike, while their heat capacity curves and underlying solid-liquid transition behavior were quite different. Since I performed no molecular dynamics simulations on these clusters, I have no direct dynamical evidence of the coexistence behavior that is an essential characteristic of homogeneous 13-atom rare gas clusters, but the J-walking and Metropolis results can be used to infer changes in the coexistence behavior for the different cluster compositions. $NeAr_{12}$ and possibly $Ne_{12}Ar$ had sufficient implicit evidence to infer they underwent coexistence, although the coexistence behavior in $Ne_{12}Ar$ was different from that of Ne_{13}. For the other clusters, though, the solid-liquid transitions were best described as a progressive evolution of isomerizations between predominately topologically distinct isomers. This progression became less continuous as the proportion of Ar atoms increased and the different sets of permutational isomers became increasingly segregated, eventually transforming into the coexistence behavior of $NeAr_{12}$ and Ar_{13}. It is interesting to note that the broadening and lowering of the heat capacity peaks as the cluster composition varied from $NeAr_{12}$ to Ne_5Ar_8, followed by the narrowing and increased peak heights from Ne_6Ar_7 to Ne_9Ar_4, were very similar to the changes in the homogeneous cluster heat capacities as the aggregate size N changed from 13 to 19.[2] The large $N = 13$ peak decreased and broadened as N increased to 16, and then narrowed and increased to the $N = 19$ peak. The magic number endpoints $N = 13$ and 19 had pronounced solid-liquid coexistence ranges, while the clusters $N = 15, 16$ and 17, which had low, broad peaks, underwent solid-liquid transitions comprised of smooth

progressions of isomerizations.

As was the case with the Ar-Kr clusters, the calculations presented here have demonstrated that the standard Metropolis algorithm is inadequate for dealing with the low-temperature behavior of heterogeneous clusters. Unlike the Ar-Kr case, though, augmenting the Metropolis method with the atom-exchange method did not improve its accuracy much for the Ne-Ar clusters. Again, the J-walking calculations for these binary clusters were more complicated than those done on similar homogeneous clusters because of the greater possibility for systematic errors corrupting the J-walker distributions. Using multiple trials from independently generated distributions helped ensure that such errors were not present. The computational overhead was mitigated by the shorter walk lengths required for J-walking to achieve the desired level of accuracy compared to the Metropolis method; for example, for the $Ne_{11}Ar_2$ heat capacity curve over the range $6 \leq T \leq 8$ K, the J-walker runs of 10^6 passes each had a level of accuracy that required runs totaling 10^8 passes for the Metropolis method to match, and even at 10^8 total passes, the Metropolis method had large systematic errors below 6 K.

Finally, it should be noted that the Ne-Ar results reported here are deficient in that they were obtained from classical simulations. Previous quantum studies of Ne clusters have shown that quantum effects play a large role in their behavior,[28] and so quantum simulations would likely be needed for a realistic treatment of Ne-Ar clusters as well, especially for the predominately Ne ones. Since my primary motivation with this study was to elucidate the effects of largely different atomic sizes and intermolecular forces on binary cluster behavior, as well as the dependence on cluster composition, the Ne-Ar clusters served primarily as a model system, and so the classical simulations were quite adequate. Quantum effects are most pronounced at lower temperatures, and for the predominately Ne clusters, much of the interesting behavior occurred at the low temperatures where quantum effects are expected to have a major impact. For example, barriers between low-lying isomers are effectively reduced in quantum simulations, and so transitions from stacked isomers to monolayer isomers in $Ne_{12}Ar$ could become dynamically accessible in quantum simulations, and the heat capacity

peak behavior thus much modified.

ACKNOWLEDGMENTS

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[40] The Savitsky-Golay algorithm was used for the data smoothing, and 2D cubic splines were used for the interpolation. These routines are implemented in the MS Windows graphics software package Axum, version 4.0.

[41] The Metropolis simulations were extended to much higher temperatures than the J-walking simulations. Although not shown in the plots in Fig. 5, the Metropolis curves for each cluster had a higher temperature peak asscociated with the cluster's dissociation region. These peaks' locations and heights depended very much on the boundary conditions imposed by the constraining spheres.

FIG. 1. Heat capacity curves for $Ne_{11}Ar_2$ clusters. The solid curves were obtained from separate J-walking runs, each using a different set of J-walker distributions; the data for each temperature were obtained from 10^6 total passes. Over most of the temperature domain, the differences between the curves are comparable to the noise levels inherent in each, indicating that the systematic errors associated with each J-walker distribution were sufficiently small in these regions. The larger differences between the curves at the low-temperature peak illustrate how sensitive the peak is to small systematic errors in the low-temperature J-walker distributions. Also included is the dashed curve obtained from standard Metropolis runs having 10^7 total passes of data accumulation at each temperature. The curve was begun at the lowest temperature using the lowest energy isomer as the initial configuration, with the final configuration at each temperature then used as the initial configuration for the next temperature. Substantial discrepancies due to quasiergodicity are evident for temperatures below 6 K, with the low-temperature peak completely absent. Augmenting standard Metropolis with the atom-exchange algorithm did not improve its low temperature performance in this case, as can be seen by the filled circles, which lie mostly on the Metropolis curve. The open circles represent results obtained from standard Metropolis runs having 10^8 total passes of data accumulation at each temperature. These are in better agreement with the J-walker results down to 6 K, but still show the same sharp drop at this temperature that the shorter Metropolis runs did. The heat capacities are in reduced units.

FIG. 2. The 13 lowest energy isomers found for $Ne_{13-n}Ar_n$ clusters ($1 \le n \le 12$), in order of increasing energy; their energies are listed in Table II. The isomers were obtained from quenches of the configurations stored in J-walker distribution files. For the predominately-Ne clusters $Ne_{12}Ar$ and $Ne_{11}Ar_2$, the global minimum corresponds to an icosahedral-like configuration having a Ne atom as the central atom, but for the predominately-Ar clusters Ne_4Ar_9 to $NeAr_{12}$, the global minimum in each case corresponds to an icosahedral-like configuration having an Ar atom as the central atom. The global minimum for each of the intermediate cases $Ne_{10}Ar_3$ to Ne_5Ar_8 is non-icosahedral.

FIG. 3. Potential energies as functions of composition for the lowest energy non-icosahedral isomers (circles) and icosahedral-like isomers (squares for Ne-core, and diamonds for Ar-core isomers). The energies in the upper plot are in reduced units of $\epsilon_{\text{Ne-Ne}}$, while the energies in the lower plot have been scaled by the composition weighted average $\epsilon_{\text{Avg}} = X_{\text{Ne}}\epsilon_{\text{Ne-Ne}} + X_{\text{Ar}}\epsilon_{\text{Ar-Ar}}$, where $X_{\text{Ne}} = n_{\text{Ne}}/(n_{\text{Ne}} + n_{\text{Ar}})$ and $X_{\text{Ar}} = 1 - X_{\text{Ne}}$. The Ne-core icosahedral-like isomers were the global minimum configurations up to $\text{Ne}_{11}\text{Ar}_2$, after which the non-icosahedral isomers became the ground state. The Ar-core icosahedral-like configurations became the ground state at Ne_4Ar_9; for clusters having fewer than 7 Ar atoms, the Ar-core icosahedral-like isomers were highly distorted, and those having fewer than 4 Ar atoms were unstable.

FIG. 4. Local potential energy minima (in reduced units) for $\text{Ne}_{13-n}\text{Ar}_n$ clusters ($0 \leq n \leq 13$). In each case, the zero energy level corresponds to the global minimum energy. The energies were obtained from quenches of the configurations stored in J-walker distribution files.

FIG. 5. Heat capacities for the binary clusters $\text{Ne}_{13-n}\text{Ar}_n$ ($1 \leq n \leq 12$). In each case, the thick curve represents the J-walking results and the thin curve the standard Metropolis results; the dots represent the results obtained using Metropolis Monte Carlo augmented with the atom-exchange algorithm. Large discrepancies between the Metropolis and J-walking results can be seen to occur at lower temperatures for all the clusters except for NeAr_{12}. The atom-exchange method showed some improvement over the standard Metropolis method, but still had large deviations from the J-walking results. For the predominately Ar clusters $\text{Ne}_3\text{Ar}_{10}$ to NeAr_{12}, the large high-temperature peaks correspond to solid-liquid transitions, but for the other clusters, the peaks are so broad that they encompass not only the solid-liquid transition, but also the dissociation of the Ne component at the higher temperatures. The Ne_{12}Ar peak and the very small low-temperature peaks seen in $\text{Ne}_{11}\text{Ar}_2$, Ne_9Ar_4, Ne_8Ar_5, Ne_6Ar_7 and Ne_5Ar_8 are due to low-lying isomers whose energies are close to the global minimum energies. Only NeAr_{12} has a heat capacity curve similar to that of its homogeneous counterpart.

FIG. 6. Trends in the higher temperature heat capacity peak parameters. The top plot shows the peak temperatures as a function of cluster composition, while the middle plot shows the peak heights as a function of composition. The bottom plot depicts the peak heights as a function of the peak temperature. The uncertainties in the peak heights and temperatures are smaller than the symbol size. The predominately Ne clusters ($n_{Ne} > 9$) and the predominately Ar clusters ($n_{Ar} > 9$) have parameter trends much different than that of the other clusters. The peak temperature and height for each cluster also are listed in Table III.

FIG. 7. Potential energy curves as functions of temperature for $Ne_{13-n}Ar_n$ clusters ($0 \leq n \leq 13$). The curves were obtained from the J-walking simulations.

FIG. 8. Quench results for the predominately Ne clusters. These were obtained by periodically quenching cluster configurations by steepest descent every 1000 passes during one of the J-walker runs, giving 1000 quenched configurations for each temperature. In each case, results for the six lowest energy isomers shown in Fig. 2 are plotted, and the solid curve represents the sum of all the other isomers. The dashed vertical lines in each plot indicate the heat capacity peak temperatures.

FIG. 9. J-walker quench results for the clusters Ne_8Ar_5 to Ne_5Ar_8.

FIG. 10. J-walker quench results for the predominately Ar clusters. The $NeAr_{12}$ curves are similar to those of Ar_{13}.

FIG. 11. Metropolis quench results for $Ne_{12}Ar$ clusters. The solid symbols represent the results obtained from Metropolis simulations that were started from the global minimum configuration at 0.1 K, with the temperature increased in increments of 0.1 K, while the open symbols represent the results obtained from similar runs started at 10 K, with the temperature decreased in increments of 0.1 K. The sets of curves agree with each other, and agree with the J-walking curves for $Ne_{12}Ar$ shown in Fig. 8 only for temperatures greater than 6.2 K. The Metropolis simulations run in the direction of decreasing temperature did not reach the lowest energy isomer as the temperature approached zero.

TABLES

TABLE I. Lennard-Jones parameters used in the calculations. The Ne-Ne and Ar-Ar parameters were obtained from Ref. 30. The Ne-Ar parameters were obtained from the usual Lorentz-Berthelot mixing rules, with $\epsilon_{\text{Ne-Ar}} = (\epsilon_{\text{Ne-Ne}} \epsilon_{\text{Ar-Ar}})^{1/2}$ and $\sigma_{\text{Ne-Ar}} = \frac{1}{2}(\sigma_{\text{Ne-Ne}} + \sigma_{\text{Ar-Ar}})$.

Parameter	Ne-Ne	Ne-Ar	Ar-Ar
ϵ/K	35.60	65.20	119.4
$\sigma/\text{Å}$	2.749	3.077	3.405

TABLE II. Potential energies for the thirteen lowest-energy equilibrium configurations shown in Fig. 2. These values were obtained from quench studies of the configurations stored in the J-walker distribution files or by minimizing the various permutations of icosahedral configurations. The energies are expressed in reduced units of $-\epsilon_{\text{Ne-Ne}}$.

Isomer	Ne_{13}	$Ne_{12}Ar$	$Ne_{11}Ar_2$	$Ne_{10}Ar_3$	Ne_9Ar_4	Ne_8Ar_5	Ne_7Ar_6
0	44.32680	50.14737	56.57433	64.24192	71.38399	78.86406	86.39936
1	41.47198	48.83695	56.52063	63.72413	71.08382	78.66373	85.83742
2	41.44460	48.76841	56.06123	63.71574	70.94101	78.52868	85.81146
3	41.39440	48.76223	56.03686	63.66647	70.93143	78.51267	85.76317
4	40.75851	48.71912	55.93749	63.59504	70.85554	78.46705	85.63794
5	40.72846	48.65682	55.81092	63.59501	70.77891	78.04509	85.62603
6	40.71041	48.38159	55.79632	63.19284	70.75207	78.02281	85.56162
7	40.67380	48.32417	55.70070	63.10945	70.74139	77.99609	85.55390
8	40.67017	48.31641	55.69579	63.05431	70.72857	77.93368	85.50783
9	40.61547	48.24531	55.64982	63.04676	70.72729	77.88402	85.49314
10	40.60458	48.18147	55.61569	63.01544	70.68951	77.88031	85.41050
11	40.54129	48.11949	55.61427	62.96995	70.67538	77.84458	85.39834
12	40.43333	48.11635	55.60919	62.95865	70.65142	77.73255	85.36450
Isomer	Ar_{13}	$NeAr_{12}$	Ne_2Ar_{11}	Ne_3Ar_{10}	Ne_4Ar_9	Ne_5Ar_8	Ne_6Ar_7
0	148.66910	137.68293	127.58029	118.43464	109.36661	100.77911	93.73315
1	139.09422	133.68855	126.78465	117.49640	108.72718	100.67782	93.61382
2	139.00238	133.57037	126.72343	116.79154	108.59267	100.67727	93.53146
3	138.83402	133.53295	124.53811	116.72628	108.52706	100.65515	93.47289
4	136.70131	133.46282	124.44729	116.54890	108.46116	100.63225	93.41254
5	136.60051	130.36349	124.43270	116.51740	108.45875	100.62103	93.41221
6	136.53996	129.95629	124.41134	116.50550	108.44127	100.56415	93.38494
7	136.41718	129.92105	124.38340	116.46722	108.41135	100.56237	93.33902

8	136.40501	129.86693	124.34131	116.44073	108.40618	100.56091	93.10541
9	136.22154	129.80847	124.34068	116.42079	108.35227	100.55547	93.07193
10	136.18504	129.70576	124.32050	116.20818	108.25224	100.51264	92.99134
11	135.97277	129.70212	123.66593	115.98123	107.99351	100.50910	92.94263
12	135.61066	129.69684	123.65838	115.74204	107.90823	100.47166	92.87926

TABLE III. Heat capacity peak parameters for 13-atom Ne-Ar clusters. These values were obtained by smoothing and interpolating the J-walking data shown in Fig. 5. The Ne_{13} and Ar_{13} values were obtained by scaling the values in reported Ref. 1. The heat capacity uncertainty estimates are averages of single standard deviations of the points near the peaks.

	Lower temperature peak		Higher temperature peak	
	T_{peak} (K)	$\langle C_V^* \rangle_{\text{peak}}$	T_{peak} (K)	$\langle C_V^* \rangle_{\text{peak}}$
Ne_{13}			10.15 ±0.02	118.5 ±0.6
$Ne_{12}Ar$			5.20 ±0.03	67.1 ±0.9
$Ne_{11}Ar_2$	0.37 ±0.03	41.1 ±0.7	8.92 ±0.14	59.2 ±0.3
$Ne_{10}Ar_3$			6.76 ±0.03	58.5 ±0.5
Ne_9Ar_4	3.40 ±0.02	47.4 ±0.7	24.27 ±0.34	79.6 ±0.3
Ne_8Ar_5	2.02 ±0.02	40.6 ±0.3	24.46 ±0.17	75.4 ±0.4
Ne_7Ar_6			25.62 ±0.20	71.7 ±0.4
Ne_6Ar_7	1.69 ±0.06	38.9 ±0.3	24.83 ±0.35	69.3 ±0.4
Ne_5Ar_8	1.63 ±0.10	39.8 ±0.4	25.40 ±0.33	67.3 ±0.3
Ne_4Ar_9			22.42 ±0.05	68.2 ±0.5
Ne_3Ar_{10}			22.01 ±0.31	73.9 ±0.4
Ne_2Ar_{11}			25.49 ±0.14	84.2 ±0.7
$NeAr_{12}$			29.68 ±0.11	95.2 ±0.5
Ar_{13}			34.05 ±0.07	118.0 ±0.6

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